

10-24-00

EL465851515

PTO/SB/05 (4/98)

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Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

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**UTILITY
PATENT APPLICATION
TRANSMITTAL**

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No. MI22-1544

First Inventor or Application Identifier Guy T. Blalock

Title Plasma Etching Methods

Express Mail Label No. EL465851515

PTO
U.S. PTO
09/27/98
10/02/00**APPLICATION ELEMENTS**

See MPEP chapter 600 concerning utility patent application contents.

1. ☒ * Fee Transmittal Form (e.g., PTO/SB/17)
(Submit an original and a duplicate for fee processing)2. ☒ Specification [Total Pages 24]
(preferred arrangement set forth below)

- Descriptive title of the Invention
- Cross References to Related Applications
- Statement Regarding Fed sponsored R & D
- Reference to Microfiche Appendix
- Background of the Invention
- Brief Summary of the Invention
- Brief Description of the Drawings (if filed)
- Detailed Description
- Claim(s)
- Abstract of the Disclosure

3. ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets 1]

4. Oath or Declaration [Total Pages 3]

a. ☐ Newly executed (original or copy)b. ☒ Copy from a prior application (37 C.F.R. § 1.63(d))
(for continuation/divisional with Box 16 completed)i. ☐ **DELETION OF INVENTOR(S)**
Signed statement attached deleting
inventor(s) named in the prior application,
see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).*** NOTE FOR ITEMS 1 & 13 IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY
FEES, A SMALL ENTITY STATEMENT IS REQUIRED (37 C.F.R. § 1.27), EXCEPT
IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).****ADDRESS TO:** Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

- 5. ☐ Microfiche Computer Program (Appendix)
- 6. Nucleotide and/or Amino Acid Sequence Submission
(if applicable, all necessary)
 - a. ☐ Computer Readable Copy
 - b. ☐ Paper Copy (identical to computer copy)
 - c. ☐ Statement verifying identity of above copies

ACCOMPANYING APPLICATION PARTS

- 7. ☐ Assignment Papers (cover sheet & document(s))
- 8. ☐ 37 C.F.R. § 3.73(b) Statement ☐ Power of Attorney
(when there is an assignee)
- 9. ☐ English Translation Document (if applicable)
- 10. ☒ Information Disclosure Statement (IDS)/PTO-1449 ☐ Copies of IDS Citations
- 11. ☒ Preliminary Amendment
- 12. ☒ Return Receipt Postcard (MPEP 503)
(Should be specifically itemized)
- 13. ☐ * Small Entity Statement(s) ☐ Statement filed in prior application
(PTO/SB/09-12) Status still proper and desired
- 14. ☐ Certified Copy of Priority Document(s)
(if foreign priority is claimed)
- 15. ☒ Other: \$1472.00 check

16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:☒ Continuation ☐ Divisional ☐ Continuation-in-part (CIP)

of prior application No: 09/141,775

Prior application information: Examiner L. Vinh

Group / Art Unit: 1765

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.**17. CORRESPONDENCE ADDRESS**☒ Customer Number or Bar Code Label

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or ☐ Correspondence address below

(Insert Customer No. or Attach bar code label here)

Name

Address

City

State

Zip Code

Country

Telephone

Fax

Name (Print/Type)

Bernard Berman

Registration No. (Attorney/Agent)

37,279

Signature

Bernard Berman

Date

Oct 2, 2000

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EL465851515

PTO/SB/47 (42/99)

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FEE TRANSMITTAL for FY 1999

Patent fees are subject to annual revision.

Small Entity payments must be supported by a small entity statement, otherwise large entity fees must be paid. See Forms PTO/SB/09-12.

TOTAL AMOUNT OF PAYMENT (\$) 1472.00

Complete if Known

Application Number _____
 Filing Date _____
 First Named Inventor Guy T. Blalock
 Examiner Name _____
 Group / Art Unit _____
 Attorney Docket No. MI22-1544

PTO
09/677478
10702/00

METHOD OF PAYMENT (check one)

1. ☒ The Commissioner is hereby authorized to charge indicated fees and credit any over payments to:

Deposit
Account
Number
Deposit
Account
Name

23-0925

Wells, St. John et al.

- ☒ Charge Any Additional
Fee Required Under
37 CFR 1.16 and 1.17

2. ☒ Payment Enclosed:

☒ Check ☐ Money Order ☐ Other

FEE CALCULATION

1. BASIC FILING FEE

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid
101 760 201 380		Utility filing fee	710
106 310 206 155		Design filing fee	
107 480 207 240		Plant filing fee	
108 760 208 380		Reissue filing fee	
114 150 214 75		Provisional filing fee	

SUBTOTAL (1) (\$) 710.00

2. EXTRA CLAIM FEES

Total Claims	Extra Claims	Fee from below	Fee Paid
49	29	18	522
Independent Claims	6	80	240
Multiple Dependent			0.00

**or number previously paid, if greater; For Reissues, see below

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid
103 18 203 9		Claims in excess of 20	
102 78 202 39		Independent claims in excess of 3	
104 260 204 130		Multiple dependent claim, if not paid	
109 78 209 39		** Reissue independent claims over original patent	
110 18 210 9		** Reissue claims in excess of 20 and over original patent	

SUBTOTAL (2) (\$) 762.00

FEE CALCULATION (continued)

3. ADDITIONAL FEES

Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid
105 130 205 65		Surcharge - late filing fee or oath	0.00
127 50 227 25		Surcharge - late provisional filing fee or cover sheet.	0.00
139 130 139 130		Non-English specification	0.00
147 2,520 147 2,520		For filing a request for reexamination	0.00
112 920* 112 920*		Requesting publication of SIR prior to Examiner action	0.00
113 1,840* 113 1,840*		Requesting publication of SIR after Examiner action	0.00
115 110 215 55		Extension for reply within first month	0.00
116 380 216 190		Extension for reply within second month	0.00
117 870 217 435		Extension for reply within third month	0.00
118 1,360 218 680		Extension for reply within fourth month	0.00
128 1,850 228 925		Extension for reply within fifth month	0.00
119 300 219 150		Notice of Appeal	0.00
120 300 220 150		Filing a brief in support of an appeal	0.00
121 260 221 130		Request for oral hearing	0.00
138 1,510 138 1,510		Petition to institute a public use proceeding	0.00
140 110 240 55		Petition to revive - unavoidable	0.00
141 1,210 241 605		Petition to revive - unintentional	0.00
142 1,210 242 605		Utility issue fee (or reissue)	0.00
143 430 243 215		Design issue fee	0.00
144 580 244 290		Plant issue fee	0.00
122 130 122 130		Petitions to the Commissioner	0.00
123 50 123 50		Petitions related to provisional applications	0.00
126 240 126 240		Submission of Information Disclosure Stmt	0.00
581 40 581 40		Recording each patent assignment per property (times number of properties)	0.00
146 760 246 380		Filing a submission after final rejection (37 CFR 1.129(a))	0.00
149 760 249 380		For each additional invention to be examined (37 CFR 1.129(b))	0.00
		Other fee (specify) _____	0.00
		Other fee (specify) _____	0.00

*Reduced by Basic Filing Fee Paid

SUBTOTAL (3) (\$) 0.00

SUBMITTED BY

Typed or
Printed Name

Bernard Berman

Signature

Bernard Berman

Date

Oct 2, 2000

Complete (if applicable)

Reg. Number

37,279

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Priority Application Serial No. 09/141,775
Priority Filing Date August 27, 1998
Inventor Guy T. Blalock et al.
Priority Group Art Unit 1765
Priority Examiner L. Vinh
Attorney's Docket No. MI22-1544
Title: Plasma Etching Methods

PRELIMINARY AMENDMENT

To: Box Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231

From: Bernard Berman (Tel. 509-624-4276; Fax 509-838-3424)
Wells, St. John, Roberts, Gregory & Matkin P.S.
601 W. First Avenue, Suite 1300
Spokane, WA 99201-3828

Sir:

Please enter the following amendments prior to examining the above-identified application.

AMENDMENTS

In the Specification

At p. 1, before the "Technical Field" section, please replace the existing Related Applications section with the following:

--RELATED PATENT DATA

This patent is a continuation application of U.S. Patent Application Serial No. 09/141,775, which was filed on August 27, 1998, entitled "Plasma Etching Methods," naming Guy T. Blalock, David S. Becker, and

Kevin G. Donohoe as inventors, and which is now U.S. Patent No. _____, the disclosure of which is incorporated by reference.

At page 7, line 23 before "conducted" insert --is--.

In the Claims:

Cancel claims 8, 9, 14, 15, 29, 43, 51 and 52 without prejudice.

Pending Claims 1-7, 10-13, 16-28, 30-42, 44-50 and 53-57 are presented hereinbelow for the Examiner's benefit.

1. A plasma etching method comprising:

forming a polymer comprising carbon and a halogen over at least some internal surfaces of a plasma etch chamber; and

after forming the polymer, plasma etching using a gas effective to etch polymer from chamber internal surfaces; the gas having a hydrogen component effective to form a gaseous hydrogen halide from halogen liberated from the polymer.

2. The plasma etching method of claim 1 wherein the halogen is selected from the group consisting of fluorine, chlorine and mixtures thereof.

1 3. The plasma etching method of claim 1 wherein the halogen
2 comprises fluorine.

3
4 4. The plasma etching method of claim 1 wherein the gas also
5 comprises an oxygen component.

6
7 5. The plasma etching method of claim 1 wherein the gas also
8 comprises O₂.

9
10 6. The plasma etching method of claim 1 wherein the hydrogen
11 component comprises NH₃.

12
13 7. The plasma etching method of claim 1 wherein the hydrogen
14 component comprises H₂.

15
16 10. A plasma etching method comprising:
17 forming a polymer comprising carbon and a halogen over at least
18 some internal surfaces of a plasma etch chamber; and
19 after forming the polymer, plasma etching using a gas effective to
20 etch polymer from chamber internal surfaces; the gas comprising a
21 carbon compound effective to getter the halogen from the etched
22 polymer.
23

1 11. The plasma etching method of claim 10 wherein the gettering
2 comprises forming a gaseous hydrogen halide from the etched halogen.
3

4 12. The plasma etching method of claim 10 wherein the gettering
5 comprises forming a gaseous COA_x compound, where A is the etched
6 halogen.
7

8 13. The plasma etching method of claim 10 wherein the carbon
9 compound comprises a hydrocarbon.
10

11 16. The plasma etching method of claim 10 wherein the carbon
12 compound comprises a C-O bond.
13

14 17. The plasma etching method of claim 10 wherein the carbon
15 compound comprises CO.
16

17 18. The plasma etching method of claim 10 wherein the carbon
18 compound comprises CO formed from CO_2 injected into the chamber.
19

20 19. The plasma etching method of claim 10 wherein the halogen
21 comprises fluorine.
22
23

1 20. The plasma etching method of claim 10 wherein the gas also
2 comprises an oxygen component.

3
4 21. A plasma etching method comprising:
5 positioning a semiconductor wafer on a wafer receiver within a
6 plasma etch chamber;

7 first plasma etching material on the semiconductor wafer with a
8 gas comprising carbon and a halogen, a polymer comprising carbon and
9 the halogen forming over at least some internal surfaces of the plasma
10 etch chamber during the first plasma etching; and

11 after the first plasma etching and with the wafer on the wafer
12 receiver, second plasma etching using a gas effective to etch polymer
13 from chamber internal surfaces and getter halogen liberated from the
14 polymer to restrict further etching of the material on the semiconductor
15 wafer during the second plasma etching.

16
17 22. The plasma etching method of claim 21 wherein the receiver
18 is biased during the first plasma etching and provided at ground or
19 floating potential during the second plasma etching.

20
21 23. The plasma etching method of claim 21 wherein the gas
22 comprises hydrogen which combines with the halogen during the second
23 plasma etching to form a gaseous hydrogen halide.

1 24. The plasma etching method of claim 21 wherein the second
2 etching is conducted with a temperature of the receiver provided at from
3 about -10°C to about 40°C and at a chamber pressure of from about 30
4 mTorr to about 5 Torr.

5
6 25. The plasma etching method of claim 21 wherein the halogen
7 comprises fluorine.

8
9 26. The plasma etching method of claim 21 wherein the gas
10 comprises an oxygen component.

11
12 27. The plasma etching method of claim 21 wherein the gas
13 comprises NH_3 , with hydrogen from the NH_3 combining with the halogen
14 during the second plasma etching to form a gaseous hydrogen halide.

15
16 28. The plasma etching method of claim 21 wherein the gas
17 comprises H_2 which combines with the halogen during the second plasma
18 etching to form a gaseous hydrogen halide.

1 30. The plasma etching method of claim 21 wherein the first and
2 second plasma etchings are conducted at subatmospheric pressure, and
3 the wafer remaining *in situ* on the receiver intermediate the first and
4 second etchings, and maintaining the chamber at a subatmospheric
5 pressure at all time intermediate the first and second plasma etchings.
6

7 31. The plasma etching method of claim 21 wherein the gettering
8 comprises forming a gaseous COA_x compound, where A is the etched
9 halogen.
10

11 32. The plasma etching method of claim 21 wherein the gas
12 comprises a carbon compound effective for the gettering.
13

14 33. The plasma etching method of claim 32 wherein the carbon
15 compound comprises a hydrocarbon.
16

17 34. The plasma etching method of claim 32 wherein the carbon
18 compound comprises a C-O bond.
19

20 35. The plasma etching method of claim 32 wherein the carbon
21 compound comprises CO.
22
23

1 36. A plasma etching method comprising:

2 positioning a semiconductor wafer on a wafer receiver within a
3 plasma etch chamber, the semiconductor wafer having a photoresist layer
4 formed thereon;

5 first plasma etching material on the semiconductor wafer through
6 openings formed in the photoresist layer with a gas comprising carbon
7 and a halogen, a polymer comprising carbon and the halogen forming
8 over at least some internal surfaces of the plasma etch chamber during
9 the first plasma etching; and

10 after the first plasma etching and with the wafer on the wafer
11 receiver, second plasma etching using a gas having one or more
12 components effective to etch photoresist from the substrate and polymer
13 from chamber internal surfaces and getter halogen liberated from the
14 polymer to restrict further etching of the material on the semiconductor
15 wafer during the second plasma etching.

16
17 37. The plasma etching method of claim 36 one of the gas
18 components comprises hydrogen which combines with the halogen during
19 the second plasma etching to form a gaseous hydrogen halide.

20
21 38. The plasma etching method of claim 36 wherein one of the
22 gas components comprises O₂ and another is hydrogen atom containing.
23

1 39. The plasma etching method of claim 36 wherein one of the
2 gas components comprises O_2 and another is hydrogen atom containing,
3 said one component and said another component being provided in the
4 chamber during the second plasma etching at a volumetric ratio of the
5 one to the another of at least 0.1:1.

6
7 40. The plasma etching method of claim 36 wherein the halogen
8 comprises fluorine.

9
10 41. The plasma etching method of claim 36 wherein one of the
11 gas components comprises NH_3 , with hydrogen from the NH_3 combining
12 with the halogen during the second plasma etching to form a gaseous
13 hydrogen halide.

14
15 42. The plasma etching method of claim 36 wherein one of the
16 gas components comprises H_2 which combines with the halogen during
17 the second plasma etching to form a gaseous hydrogen halide.

18
19 44. The plasma etching method of claim 36 wherein the first and
20 second plasma etchings are conducted at subatmospheric pressure, and
21 the wafer remaining *in situ* on the receiver intermediate the first and
22 second etchings, and maintaining the chamber at a subatmospheric
23 pressure at all time intermediate the first and second plasma etchings.

1 45. The plasma etching method of claim 36 wherein the gettering
2 comprises forming a gaseous COA_x compound, where A is the etched
3 halogen.

4
5 46. The plasma etching method of claim 36 wherein the gas
6 comprises a carbon compound effective for the gettering.

1 47. A plasma etching method comprising:

2 positioning a semiconductor wafer on an electrostatic chuck within
3 an inductively coupled plasma etch chamber, the semiconductor wafer
4 having a photoresist layer formed on an insulative oxide layer, the
5 photoresist layer having contact opening patterns formed therethrough;

6 first plasma etching contact openings within the insulative oxide on
7 the semiconductor wafer through the contact opening patterns formed in
8 the photoresist layer with a gas comprising carbon and fluorine, a
9 polymer comprising carbon and fluorine forming over at least some
10 internal surfaces of the plasma etch chamber during the first plasma
11 etching; and

12 after the first plasma etching and with the wafer on the
13 electrostatic chuck, providing the electrostatic chuck at ground or floating
14 potential while second plasma etching using a gas comprising an oxygen
15 component and a hydrogen component effective to etch photoresist from
16 the substrate and polymer from chamber internal surfaces, and forming
17 HF during the second plasma etching from fluorine liberated from the
18 polymer to restrict widening of the contact openings formed in the
19 insulative oxide resulting from further etching of the material on the
20 semiconductor wafer during the second plasma etching.

21
22 48. The plasma etching method of claim 47 wherein the oxygen
23 comprises O₂.

1 49. The plasma etching method of claim 47 wherein the hydrogen
2 component comprises NH_3 .

3
4 50. The plasma etching method of claim 47 wherein the hydrogen
5 component comprises H_2 .

6
7 53. The plasma etching method of claim 47 wherein the first and
8 second plasma etchings are conducted at subatmospheric pressure, and
9 the wafer remaining *in situ* on the electrostatic chuck intermediate the
10 first and second etchings, and maintaining the chamber at a
11 subatmospheric pressure at all time intermediate the first and second
12 plasma etchings.

1 54. A plasma etching method comprising:

2 positioning a semiconductor wafer on an electrostatic chuck within
3 an inductively coupled plasma etch chamber, the semiconductor wafer
4 having a photoresist layer formed on an insulative oxide layer, the
5 photoresist layer having contact opening patterns formed therethrough;

6 first plasma etching contact openings within the insulative oxide on
7 the semiconductor wafer through the contact opening patterns formed in
8 the photoresist layer with a gas comprising carbon and fluorine, a
9 polymer comprising carbon and fluorine forming over at least some
10 internal surfaces of the plasma etch chamber during the first plasma
11 etching; and

12 after the first plasma etching and with the wafer on the
13 electrostatic chuck, providing the electrostatic chuck at ground or floating
14 potential while second plasma etching using a gas comprising an oxygen
15 component and a carbon component effective to etch photoresist from
16 the substrate and polymer from chamber internal surfaces, and gettering
17 fluorine liberated from the polymer during the second plasma etching
18 with the carbon component to restrict widening of the contact openings
19 formed in the insulative oxide resulting from further etching of the
20 material on the semiconductor wafer during the second plasma etching.

21
22 55. The plasma etching method of claim 54 wherein the gettering
23 comprises forming a gaseous hydrogen halide from the etched halogen.

1 56. The plasma etching method of claim 54 wherein the gettering
2 comprises forming a gaseous COA_x compound, where A is the etched
3 halogen.

4
5 57. The plasma etching method of claim 54 wherein the carbon
6 compound comprises a C-O bond.

REMARKS

This application is a continuation application of U.S. Patent Application Serial No. 09/141,775, filed August 27, 1998. Claims 8, 9, 14, 15, 29, 43, 51 and 52 have been canceled without prejudice. Claims 1-7, 10-13, 16-28, 30-42, 44-50 and 53-57 are pending herein.

In an Office Action mailed August 25, 2000, Claims 1-7, 10-13, 16-28, 30-42, 44-50 and 53-57 were rejected under 35 U.S.C. §103(a) as being unpatentable under various combinations of Keller (U.S. Patent No. 5,644,153), Xia et al. (U.S. Patent No. 5,935,340, hereinafter "Xia") and Saito et al. (U.S. Patent No. 5,681,424, hereinafter "Saito").

The Examiner alleged that the plasma etching method disclosed by Keller encompass plasma etching a semiconductor wafer with a plasma etching material where a polymer of carbon and halogen are formed over an etching chamber's internal surfaces. The Examiner further alleged that the method of Keller also disclosed plasma etching with a gas effective to etch/clean the polymer formed on the chamber's surfaces, although such effective gas does not disclose that a gaseous hydrogen halide product of such etch/clean is formed. Rather the Examiner alleges that Xia disclosed such an effective gas, specifically at column 59, lines 47-50 and alleged further, that one skilled in the art would have found it obvious to use Keller's gas having a hydrogen component to form a hydrogen halide in view of Xia. Applicant DISAGREES.

1 As the Examiner admitted on page 3, line 2 of the
2 above-referenced Office Action, Keller's gas having a hydrogen component
3 is HBr, a gas containing both hydrogen and a halogen, specifically
4 bromine. Hence Applicant respectfully asserts that such a gas cannot be
5 effective by itself to remove a halogen from the polymer as the
6 stoichiometry of HBr dictates that for each hydrogen introduced, a
7 halogen is introduced, therefore there can be NO net removal of halogen
8 using such a gas. Rather, if such a gas were to react with a halogen
9 contained within a polymer, at best the halogen of the polymer would
10 only be exchanged for the bromine of the HBr.

11 In addition, Applicant notes that the process disclosed by Xia is
12 not a plasma etching process as described by Keller. Rather Xia
13 discloses a method for HIGH TEMPERATURE PROCESSING.
14 Specifically, the process disclosed at the portion of Xia referred to by
15 the Examiner is performed at a preferred temperature range of 550 to
16 600°C, a temperature at which the wafers being processed by Keller are
17 likely to be damaged due to the decomposition of the photoresist Keller
18 teaches is used as an etch mask. Hence, Applicant asserts that a
19 combination of Keller and Xia would NOT be obvious, as a skilled
20 practitioner of the etching arts would know that (1) HBr would not be
21 expected to cause any net reduction in halogen content as it introduces
22 as much halogen as it can remove, and (2) the high temperature process
23

1 of Xia cannot be combined with the etching process of Keller as such
2 would, at the very least, severely damage the photoresist masking layer.

3 The Examiner also refers, in the rejection of some claims, to Saito.
4 Specifically the Examiner alleges that Saito discloses the use of oxygen,
5 not disclosed in either of Keller or Xia. The Examiner then alleges that
6 it would have been obvious for one skilled in the art to combine the
7 oxygen disclosed by Saito with the method resulting from the
8 combination of Keller and Xia. Applicant DISAGREES. Keller
9 specifically teaches that the two step process disclosed is to provide
10 improved critical dimension control of the etched material. Keller
11 provides such improved control by providing a second etching step which
12 functions "to remove non-uniformities that remain after the primary etch"
13 (col. 4, lines 41-42). The second etching step has a lower etch rate,
14 with respect to the silicon nitride being etched, than the first etching
15 step (id., lines 48-49) and additionally removes most of the polymer
16 formed on the sidewalls of the etched structure during the first etching
17 step (id. lines 56-57). However, as oxygen introduced into a plasma
18 etching chamber is well known as a method for removing photoresist,
19 Applicant asserts that such an introduction in the second etching step
20 of Keller would, at the very least, remove some of the photoresist mask
21 and thus cause such second etching step to alter the critical dimension
22 of the structure formed by the etching of the first step. It is also well
23 known that the rate of such photoresist removal is enhanced by high

1 temperatures so that it is likely that the high temperatures taught by Xia
2 would dramatically increase such a removal rate. Thus, Applicant asserts
3 that rather than a combination that would be obvious to a skilled
4 practitioner, the Examiner's proposed combination would prevent the
5 method of Keller from achieving the result to which it is directed.

6 In summary, Applicant presents Claims 1-7, 10-13, 16-28, 30-42,
7 44-50 and 53-57 for consideration in this Continuation Application.
8 Additionally, Applicant respectfully asserts that in view of the remarks
9 presented above, a rejection of such claims based on ANY combination
10 of Keller, Xia and Saito is inappropriate as such combinations cannot be
11 suggested where they prevent the result sought by any one of the
12 references cited. Such has been shown above. Applicant therefore
13 asserts that such claims are in condition for allowance as presented,
14 which action is earnestly sought.

15
16 Respectfully submitted,

17
18 Dated: Oct 2, 2000

By: Bernard Berman

Bernard Berman
Reg. No. 37,279

EL 5483 1987

EL 465851515

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION FOR LETTERS PATENT

* * * * *

Plasma Etching Methods

* * * * *

INVENTORS

**Guy T. Blalock
David S. Becker
Kevin G. Donohoe**

ATTORNEY'S DOCKET NO. MI22-776

PLASMA ETCHING METHODS

TECHNICAL FIELD

This invention relates to plasma etching methods.

BACKGROUND OF THE INVENTION

Plasma etchers are commonly used in semiconductor wafer processing for fabrication of contact openings through insulating layers. A photoresist layer having contact opening patterns formed therethrough is typically formed over an insulative oxide layer, such as SiO_2 and doped SiO_2 . An oxide etching gas, for example CF_4 , is provided within the etcher and a plasma generated therefrom over the wafer or wafers being processed. The etching gas chemistry in combination with the plasma is ideally chosen to be highly selective to etch the insulating material through the photoresist openings in a highly anisotropic manner without appreciably etching the photoresist itself. A greater degree of anisotropy is typically obtained with such dry plasma etchings of contact openings than would otherwise occur with wet etching techniques.

One type of plasma etcher includes inductively coupled etching reactors. Such typically include an inductive plasma generating source coiled about or at the top of the reactor chamber and an electrostatic chuck within the chamber atop which one or more wafers being processed lies. The electrostatic chuck can be selectively biased as determined by the operator. Unfortunately when utilizing etching components having both carbon and fluorine, particularly in inductively

coupled etching reactors, a halocarbon polymer develops over much of the internal reactor sidewall surfaces. This polymer continually grows in thickness with successive processing. Due to instabilities in the polymer film, the films are prone to flaking causing particulate contamination. In addition, the build-up of these films can produce process instabilities which are desirably avoided.

The typical prior art process for cleaning this polymer material from the reactor employs a plasma etch utilizing O_2 as the etching gas. It is desirable that this clean occur at the conclusion of etching of the wafer while the wafer or wafers remain *in situ* within the reactor chamber. This both protects the electrostatic chuck (which is sensitive to particulate contamination) during the clean etch, and also maximizes throughput of the wafers being processed. An added benefit is obtained in that the oxygen plasma generated during the clean also has the effect of stripping the photoresist from the over the previously etched wafer.

However in the process of doing this reactor clean etch, there is an approximate 0.025 micron or greater loss in the lateral direction of the contact. In otherwords, the contact openings within the insulating layer are effectively widened from the opening dimensions as initially formed. This results in an inherent increase in the critical dimension of the circuitry design. As contact openings become smaller, it is not expected that the photolithography processing will be able to adjust in further increments of size to compensate for this critical dimension loss.

Accordingly, it would be desirable to develop plasma etching methods which can be used to minimize critical dimension loss of contact openings, and/or achieve suitable reactor cleaning to remove the polymer from the internal surfaces of the etching chamber. Although the invention was motivated from this perspective, the artisan will appreciate other possible uses with the invention only be limited by the accompanying claims appropriately interpreted in accordance with the Doctrine of Equivalents.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a diagrammatic view of a plasma etcher utilized at one processing step in accordance with the invention.

Fig. 2 is a view of the Fig. 1 apparatus and wafer at a processing step subsequent to that depicted by Fig. 1.

SUMMARY OF THE INVENTION

In but one aspect of the invention, a plasma etching method includes forming a polymer comprising carbon and a halogen over at least some internal surfaces of a plasma etch chamber. After forming the polymer, plasma etching is conducted using a gas which is effective to etch polymer from chamber internal surfaces. In one implementation, the gas has a hydrogen component effective to form a gaseous hydrogen halide from halogen liberated from the polymer. The hydrogen component is preferably one or more of H_2 , NH_3 and CH_4 . The conversion of the halogen, released from the clean into a hydrogen halide, renders it substantially ineffective in etching the substrate and thus reduces the critical dimension loss. In one implementation, the gas comprises a carbon component effective to getter the halogen from the etched polymer.

In another implementation, a plasma etching method includes positioning a semiconductor wafer on a wafer receiver within a plasma etch chamber. First plasma etching of material on the semiconductor wafer occurs with a gas comprising carbon and a halogen. A polymer comprising carbon and the halogen forms over at least some internal surfaces of the plasma etch chamber during the first plasma etching. After the first plasma etching and with the wafer on the wafer receiver, second plasma etching is conducted using a gas effective to etch polymer from chamber internal surfaces and getter halogen liberated from the polymer to restrict further etching of the material on the

1 semiconductor wafer during the second plasma etching. The first and
2 second plasma etchings are ideally conducted at subatmospheric pressure
3 with the wafer remaining *in situ* on the receiver intermediate the first
4 and second etchings, and with the chamber maintained at some
5 subatmospheric pressure at all time intermediate the first and second
6 plasma etchings.

7 The halogen preferably comprises fluorine, chlorine or mixtures
8 thereof. The gas at least during the second etching preferably includes
9 oxygen, such as O₂.

12 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

13 This disclosure of the invention is submitted in furtherance of the
14 constitutional purposes of the U.S. Patent Laws "to promote the
15 progress of science and useful arts" (Article 1, Section 8).

16 It has been discovered that the polymer deposited on the internal
17 walls of the etching chamber includes a significant concentration of
18 fluorine. It is believed that the oxygen during the clean etching under
19 plasma condition combines with the carbon and fluorine of the polymer
20 liberated from the internal walls and forms carbon monoxide and carbon
21 dioxide plus an activated or reactive fluorine species. Unfortunately,
22 this liberated fluorine species is also apparently reactive with the silicon
23 dioxide material on the wafer, which results in more etching of such
24 material and the widening of the contact openings.

Referring to Fig. 1, a plasma etching reactor is indicated generally with reference numeral 10. Such includes sidewalls 12 having internal surfaces 14. One or more gas inlets 16 and one or more gas outlets 18 are provided relative to etching chamber 12. A pump 20 is associated with outlet 18 for exhausting and establishing desired subatmospheric pressure conditions within chamber 12 during processing.

Plasma etching reactor 10 in the described embodiment is configured as an inductively coupled plasma etcher having a wafer receiver 22 within chamber 12 in the form of an electrostatic chuck. A biasing source 24 is electrically coupled with receiver 22. An inductive plasma inducing source 26 is diagrammatically shown externally at the top of chamber 10.

In accordance with the preferred embodiment, a semiconductor wafer 30 is positioned upon wafer receiver 22 within chamber 12. Wafer 30 has previously been processed to have a photoresist layer 32 formed on an insulative oxide layer (not specifically shown) formed on the outer surface of wafer 30. Photoresist layer 32 has contact opening patterns (not specifically shown) formed therethrough which ideally outwardly expose selected portions of the underlying insulative oxide layer.

A desired vacuum pressure is established and maintained within chamber 12 utilizing vacuum pump 20. An example chamber pressure is from about 30 mTorr to about 5 Torr. Inductively coupled source 26 and chuck 22 are appropriately biased to enable establishment

of a desired plasma within and immediately over wafer 30. An example power range for inductively coupled source 26 is from 100 watts to about 2,000 watts, with wafer receiver 22 being negatively biased to an example of 100 - 400 volts. Receiver 22 can have a temperature which is allowed to float, or otherwise be established and maintained at some range, for example from about -10°C to about 40°C.

Desired etching gases are injected to within chamber 12 through inlet 16, or other inlets, to provide a desired etching gas from which an etching plasma is formed immediately over wafer 30. Such gas can comprise, for example, carbon and a halogen. An exemplary gas would be CF₄. Etching is conducted for a selected time to etch contact openings within the insulative oxide material on semiconductor wafer 30 through the contact opening patterns formed within photoresist layer 32. Unfortunately, a polymer layer 40 comprising carbon and the halogen, in this example fluorine, forms over some of internal surfaces 14 of plasma etch chamber 12 during such etching. Such polymer can also form over photoresist layer 32 (not specifically shown). Such provides but one example of forming a polymer comprising carbon and a halogen over at least some internal surfaces of a plasma etch chamber.

Referring to Fig. 2, and at the conclusion of the first plasma etching and with wafer 30 on electrostatic chuck 22, chuck 22 is ideally provided at ground or floating potential and second plasma etching is conducted using a gas effective to etch polymer from chamber internal surfaces 14. The gas ideally has one or more components effective to

etch photoresist layer 32 from substrate 30 and polymer from chamber internal surfaces 14 (both being shown as removed in Fig. 2). Further, such one or more components of the gas are selected to be effective to getter halogen liberated from the polymer to restrict further etching of the insulative oxide or other previously etched material on the semiconductor wafer during the second plasma etching.

In one example, the gettering component comprises hydrogen which combines with the halogen during the second plasma etching to form a gaseous hydrogen halide which has a low reactivity with material of the semiconductor wafer, and accordingly is withdrawn from the reactor through outlet 18. Example hydrogen atom containing gases include NH_3 , H_2 , and CH_4 . One example gas for providing the hydrogen component to the chamber is forming gas which consists essentially of N_2 at about 96% or greater and H_2 at about 4% or less, by volume.

In another example, the gettering component comprises a carbon compound. Examples include hydrocarbons, aldehydes (i.e., formaldehyde) and ketones (i.e., methyl ketone). Hydrocarbons will typically getter the halogen as a hydrogen halide. Where the carbon compound comprises a C-O bond which survives the processing, the halogen will typically be gettered as COA_x , where A is the etched halogen. One example carbon containing gettering compound having a C-O bond is CO, produced for example within the plasma from injecting CO_2 to within the reactor.

herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.

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CLAIMS:

1. A plasma etching method comprising:
forming a polymer comprising carbon and a halogen over at least
some internal surfaces of a plasma etch chamber; and
after forming the polymer, plasma etching using a gas effective to
etch polymer from chamber internal surfaces; the gas having a hydrogen
component effective to form a gaseous hydrogen halide from halogen
liberated from the polymer.
2. The plasma etching method of claim 1 wherein the halogen
is selected from the group consisting of fluorine, chlorine and mixtures
thereof.
3. The plasma etching method of claim 1 wherein the halogen
comprises fluorine.
4. The plasma etching method of claim 1 wherein the gas also
comprises an oxygen component.
5. The plasma etching method of claim 1 wherein the gas also
comprises O₂.
6. The plasma etching method of claim 1 wherein the hydrogen
component comprises NH₃.

1 7. The plasma etching method of claim 1 wherein the hydrogen
2 component comprises H₂.

3
4 8. The plasma etching method of claim 1 wherein the hydrogen
5 component comprises forming gas consisting essentially of N₂ at about
6 96% or greater and H₂ at about 4% or less, by volume.

7
8 9. The plasma etching method of claim 1 wherein the hydrogen
9 component comprises CH₄.

10
11 10. A plasma etching method comprising:
12 forming a polymer comprising carbon and a halogen over at least
13 some internal surfaces of a plasma etch chamber; and
14 after forming the polymer, plasma etching using a gas effective to
15 etch polymer from chamber internal surfaces; the gas comprising a
16 carbon compound effective to getter the halogen from the etched
17 polymer.

18
19 11. The plasma etching method of claim 10 wherein the
20 gettering comprises forming a gaseous hydrogen halide from the etched
21 halogen.

1 12. The plasma etching method of claim 10 wherein the
2 gettering comprises forming a gaseous COA_x compound, where A is the
3 etched halogen.

4
5 13. The plasma etching method of claim 10 wherein the carbon
6 compound comprises a hydrocarbon.

7
8 14. The plasma etching method of claim 10 wherein the carbon
9 compound comprises an aldehyde.

10
11 15. The plasma etching method of claim 10 wherein the carbon
12 compound comprises a ketone.

13
14 16. The plasma etching method of claim 10 wherein the carbon
15 compound comprises a C-O bond.

16
17 17. The plasma etching method of claim 10 wherein the carbon
18 compound comprises CO.

19
20 18. The plasma etching method of claim 10 wherein the carbon
21 compound comprises CO formed from CO_2 injected into the chamber.

22
23 19. The plasma etching method of claim 10 wherein the halogen
24 comprises fluorine.

1 20. The plasma etching method of claim 10 wherein the gas
2 also comprises an oxygen component.

3
4 21. A plasma etching method comprising:
5 positioning a semiconductor wafer on a wafer receiver within a
6 plasma etch chamber;

7 first plasma etching material on the semiconductor wafer with a
8 gas comprising carbon and a halogen, a polymer comprising carbon and
9 the halogen forming over at least some internal surfaces of the plasma
10 etch chamber during the first plasma etching; and

11 after the first plasma etching and with the wafer on the wafer
12 receiver, second plasma etching using a gas effective to etch polymer
13 from chamber internal surfaces and getter halogen liberated from the
14 polymer to restrict further etching of the material on the semiconductor
15 wafer during the second plasma etching.

16
17 22. The plasma etching method of claim 21 wherein the receiver
18 is biased during the first plasma etching and provided at ground or
19 floating potential during the second plasma etching.

20
21 23. The plasma etching method of claim 21 wherein the gas
22 comprises hydrogen which combines with the halogen during the second
23 plasma etching to form a gaseous hydrogen halide.

1 24. The plasma etching method of claim 21 wherein the second
2 etching is conducted with a temperature of the receiver provided at
3 from about -10°C to about 40°C and at a chamber pressure of from
4 about 30 mTorr to about 5 Torr.

5
6 25. The plasma etching method of claim 21 wherein the halogen
7 comprises fluorine.

8
9 26. The plasma etching method of claim 21 wherein the gas
10 comprises an oxygen component.

11
12 27. The plasma etching method of claim 21 wherein the gas
13 comprises NH_3 , with hydrogen from the NH_3 combining with the
14 halogen during the second plasma etching to form a gaseous hydrogen
15 halide.

16
17 28. The plasma etching method of claim 21 wherein the gas
18 comprises H_2 which combines with the halogen during the second
19 plasma etching to form a gaseous hydrogen halide.

20
21 29. The plasma etching method of claim 21 wherein the gas
22 comprises CH_4 , with hydrogen from the CH_4 combining with the
23 halogen during the second plasma etching to form a gaseous hydrogen
24 halide.

1 30. The plasma etching method of claim 21 wherein the first
2 and second plasma etchings are conducted at subatmospheric pressure,
3 and the wafer remaining *in situ* on the receiver intermediate the first
4 and second etchings, and maintaining the chamber at a subatmospheric
5 pressure at all time intermediate the first and second plasma etchings.
6

7 31. The plasma etching method of claim 21 wherein the
8 gettering comprises forming a gaseous COA_x compound, where A is the
9 etched halogen.
10

11 32. The plasma etching method of claim 21 wherein the gas
12 comprises a carbon compound effective for the gettering.
13

14 33. The plasma etching method of claim 32 wherein the carbon
15 compound comprises a hydrocarbon.
16

17 34. The plasma etching method of claim 32 wherein the carbon
18 compound comprises a C-O bond.
19

20 35. The plasma etching method of claim 32 wherein the carbon
21 compound comprises CO.
22
23
24

1 36. A plasma etching method comprising:
2 positioning a semiconductor wafer on a wafer receiver within a
3 plasma etch chamber, the semiconductor wafer having a photoresist layer
4 formed thereon;

5 first plasma etching material on the semiconductor wafer through
6 openings formed in the photoresist layer with a gas comprising carbon
7 and a halogen, a polymer comprising carbon and the halogen forming
8 over at least some internal surfaces of the plasma etch chamber during
9 the first plasma etching; and

10 after the first plasma etching and with the wafer on the wafer
11 receiver, second plasma etching using a gas having one or more
12 components effective to etch photoresist from the substrate and polymer
13 from chamber internal surfaces and getter halogen liberated from the
14 polymer to restrict further etching of the material on the semiconductor
15 wafer during the second plasma etching.

16
17 37. The plasma etching method of claim 36 one of the gas
18 components comprises hydrogen which combines with the halogen during
19 the second plasma etching to form a gaseous hydrogen halide.

20
21 38. The plasma etching method of claim 36 wherein one of the
22 gas components comprises O₂ and another is hydrogen atom containing.
23
24

1 39. The plasma etching method of claim 36 wherein one of the
2 gas components comprises O_2 and another is hydrogen atom containing,
3 said one component and said another component being provided in the
4 chamber during the second plasma etching at a volumetric ratio of the
5 one to the another of at least 0.1:1.
6

7 40. The plasma etching method of claim 36 wherein the halogen
8 comprises fluorine.
9

10 41. The plasma etching method of claim 36 wherein one of the
11 gas components comprises NH_3 , with hydrogen from the NH_3 combining
12 with the halogen during the second plasma etching to form a gaseous
13 hydrogen halide.
14

15 42. The plasma etching method of claim 36 wherein one of the
16 gas components comprises H_2 which combines with the halogen during
17 the second plasma etching to form a gaseous hydrogen halide.
18

19 43. The plasma etching method of claim 36 wherein one of the
20 gas components comprises CH_4 , with hydrogen from the CH_4 combining
21 with the halogen during the second plasma etching to form a gaseous
22 hydrogen halide.
23
24

1 44. The plasma etching method of claim 36 wherein the first
2 and second plasma etchings are conducted at subatmospheric pressure,
3 and the wafer remaining *in situ* on the receiver intermediate the first
4 and second etchings, and maintaining the chamber at a subatmospheric
5 pressure at all time intermediate the first and second plasma etchings.
6

7 45. The plasma etching method of claim 36 wherein the
8 gettering comprises forming a gaseous COA_x compound, where A is the
9 etched halogen.
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11 46. The plasma etching method of claim 36 wherein the gas
12 comprises a carbon compound effective for the gettering.
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1 47. A plasma etching method comprising:

2 positioning a semiconductor wafer on an electrostatic chuck within
3 an inductively coupled plasma etch chamber, the semiconductor wafer
4 having a photoresist layer formed on an insulative oxide layer, the
5 photoresist layer having contact opening patterns formed therethrough;

6 first plasma etching contact openings within the insulative oxide
7 on the semiconductor wafer through the contact opening patterns formed
8 in the photoresist layer with a gas comprising carbon and fluorine, a
9 polymer comprising carbon and fluorine forming over at least some
10 internal surfaces of the plasma etch chamber during the first plasma
11 etching; and

12 after the first plasma etching and with the wafer on the
13 electrostatic chuck, providing the electrostatic chuck at ground or
14 floating potential while second plasma etching using a gas comprising an
15 oxygen component and a hydrogen component effective to etch
16 photoresist from the substrate and polymer from chamber internal
17 surfaces, and forming HF during the second plasma etching from
18 fluorine liberated from the polymer to restrict widening of the contact
19 openings formed in the insulative oxide resulting from further etching
20 of the material on the semiconductor wafer during the second plasma
21 etching.

22
23 48. The plasma etching method of claim 47 wherein the oxygen
24 comprises O₂.

1 49. The plasma etching method of claim 47 wherein the
2 hydrogen component comprises NH_3 .

3
4 50. The plasma etching method of claim 47 wherein the
5 hydrogen component comprises H_2 .

6
7 51. The plasma etching method of claim 47 wherein the
8 hydrogen component comprises forming gas consisting essentially of N_2
9 at about 96% or greater and H_2 at about 4% or less, by volume.

10
11 52. The plasma etching method of claim 47 wherein the
12 hydrogen component comprises CH_4 .

13
14 53. The plasma etching method of claim 47 wherein the first
15 and second plasma etchings are conducted at subatmospheric pressure,
16 and the wafer remaining *in situ* on the electrostatic chuck intermediate
17 the first and second etchings, and maintaining the chamber at a
18 subatmospheric pressure at all time intermediate the first and second
19 plasma etchings.

54. A plasma etching method comprising:

positioning a semiconductor wafer on an electrostatic chuck within an inductively coupled plasma etch chamber, the semiconductor wafer having a photoresist layer formed on an insulative oxide layer, the photoresist layer having contact opening patterns formed therethrough;

first plasma etching contact openings within the insulative oxide on the semiconductor wafer through the contact opening patterns formed in the photoresist layer with a gas comprising carbon and fluorine, a polymer comprising carbon and fluorine forming over at least some internal surfaces of the plasma etch chamber during the first plasma etching; and

after the first plasma etching and with the wafer on the electrostatic chuck, providing the electrostatic chuck at ground or floating potential while second plasma etching using a gas comprising an oxygen component and a carbon component effective to etch photoresist from the substrate and polymer from chamber internal surfaces, and gettering fluorine liberated from the polymer during the second plasma etching with the carbon component to restrict widening of the contact openings formed in the insulative oxide resulting from further etching of the material on the semiconductor wafer during the second plasma etching.

1 55. The plasma etching method of claim 54 wherein the
2 gettering comprises forming a gaseous hydrogen halide from the etched
3 halogen.

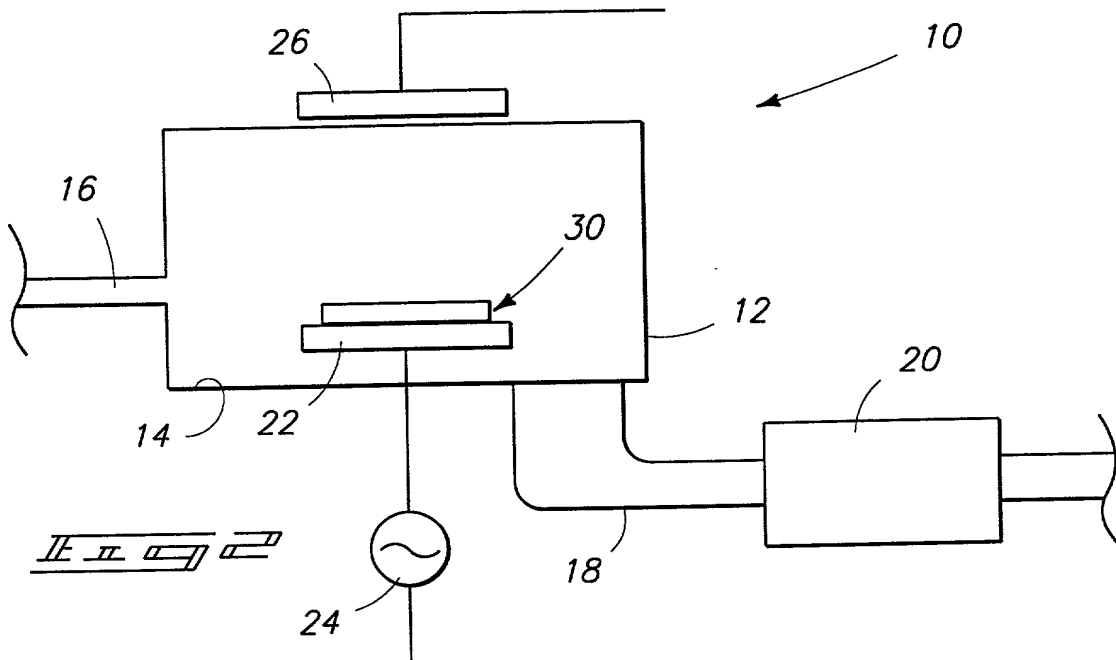
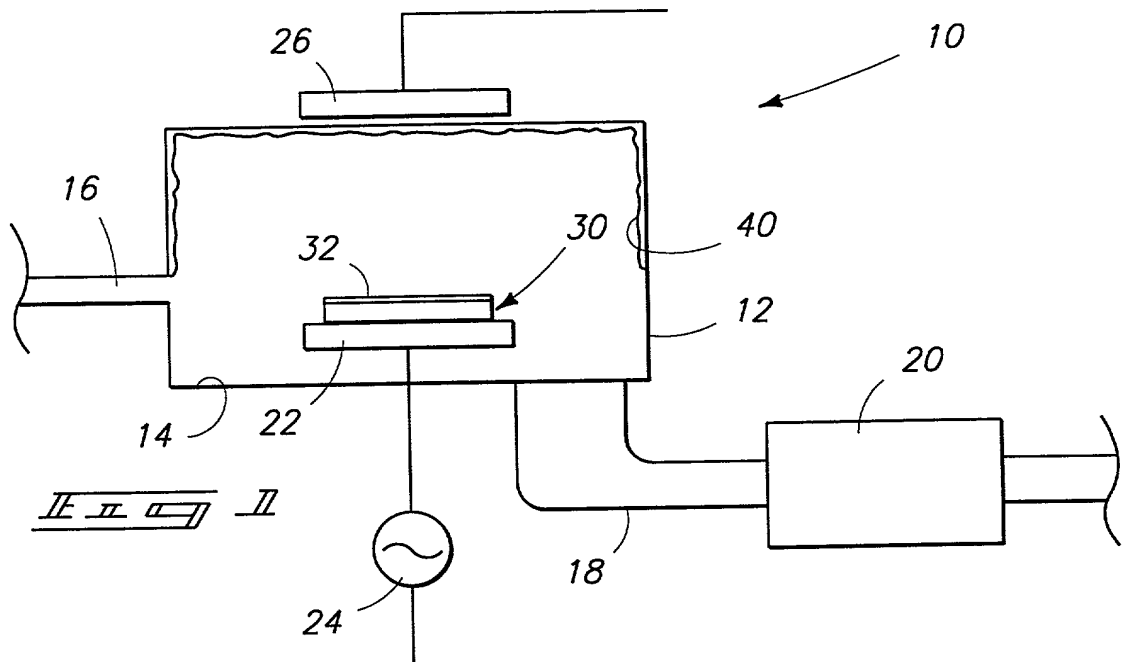
4
5 56. The plasma etching method of claim 54 wherein the
6 gettering comprises forming a gaseous COA_x compound, where A is the
7 etched halogen.

8
9 57. The plasma etching method of claim 54 wherein the carbon
10 compound comprises a C-O bond.

ABSTRACT OF THE DISCLOSURE

A plasma etching method includes forming a polymer comprising carbon and a halogen over at least some internal surfaces of a plasma etch chamber. After forming the polymer, plasma etching is conducted using a gas which is effective to etch polymer from chamber internal surfaces. In one implementation, the gas has a hydrogen component effective to form a gaseous hydrogen halide from halogen liberated from the polymer. In one implementation, the gas comprises a carbon component effective to getter the halogen from the etched polymer. In another implementation, a plasma etching method includes positioning a semiconductor wafer on a wafer receiver within a plasma etch chamber. First plasma etching of material on the semiconductor wafer occurs with a gas comprising carbon and a halogen. A polymer comprising carbon and the halogen forms over at least some internal surfaces of the plasma etch chamber during the first plasma etching. After the first plasma etching and with the wafer on the wafer receiver, second plasma etching is conducted using a gas effective to etch polymer from chamber internal surfaces and getter halogen liberated from the polymer to restrict further etching of the material on the semiconductor wafer during the second plasma etching. The first and second plasma etchings are ideally conducted at subatmospheric pressure with the wafer remaining *in situ* on the receiver intermediate the first and second etchings, and with the chamber maintained at some subatmospheric pressure at all time intermediate the first and second plasma etchings.

1/1



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DECLARATION OF JOINT INVENTORS FOR PATENT APPLICATION

As the below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled: **Plasma Etching Methods**, the specification of which is attached hereto.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations §1.56.

PRIOR FOREIGN APPLICATIONS:

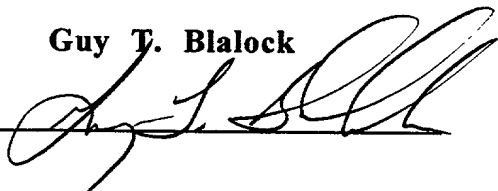
I hereby state that no applications for foreign patents or inventor's certificates have been filed prior to the date of execution of this declaration.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful

1 false statement may jeopardize the validity of the application or any
2 patent issued therefrom.

3 * * * * *

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